Fourth Annual Conference on Carbon Capture & Sequestration

Developing Potential Paths Forward Based on the Knowledge, Science and Experience to Date

Ocean Sequestration

Progress in Carrying Out Ocean CO_2 Perturbation Experiments

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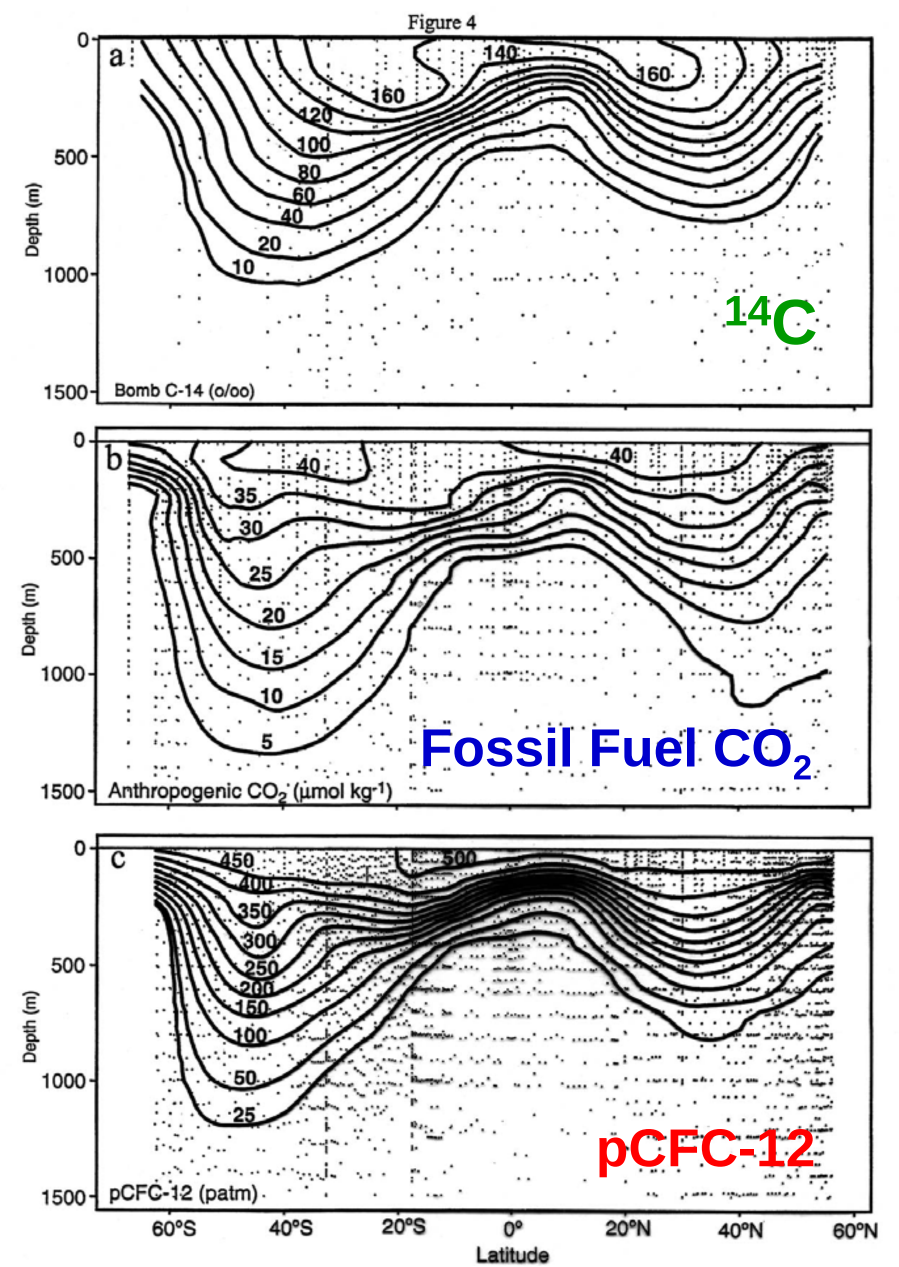
Ocean Carbon Sequestration

- First proposed by Marchetti, 1977:
  - Ocean is a big place = 1.4×10^9 km^3.
  - Already contains 50 times atmospheric burden of CO_2.
  - Seawater is strongly buffered and is slightly basic so CO_2 uptake is the "natural" reaction.
- Current situation:
  - 1/3rd of anthropogenic emissions (2 Gt C equivalent to 7 Gt CO_2) is absorbed annually.
  - As atmospheric levels rise absorption will increase.
  - ~ 80-90% of anthropogenic emissions will go there.
  - Over 500 Gt CO_2 absorbed to date.

MBARI

Ocean CO_2 "Disposal" Today



See: Sabine et al. (2004) in *Science*.

JGOFS/WOCE survey data. Pacific meridional section.

Fossil fuel signal has penetrated to >1000m. Surface values approach 50 μmol/kg (2.2 mg/kg).

The global ocean inventory of anthropogenic CO_2 from 1800 to 1999 is:

155 Gt C = 568 Gt CO_2.

Global surface ocean CO_2 disposal is now about 20-25 million tons per day.

Ocean Carbon Sequestration

- Problems:
  - Natural carbon sequestration processes are slow.
  - If uptake faster, atmospheric CO_2 rise minimized.
  - Internal circulation of ocean is slow and stratified.
  - 1/2 of anthropogenic CO_2 uptake has remained in the upper 400m of the ocean.
  - Sea surface pH already reduced by 0.1
- Technological fixes:
  - Iron fertilization to enhance biological pump.
  - Purposeful sequestration by industrial means.

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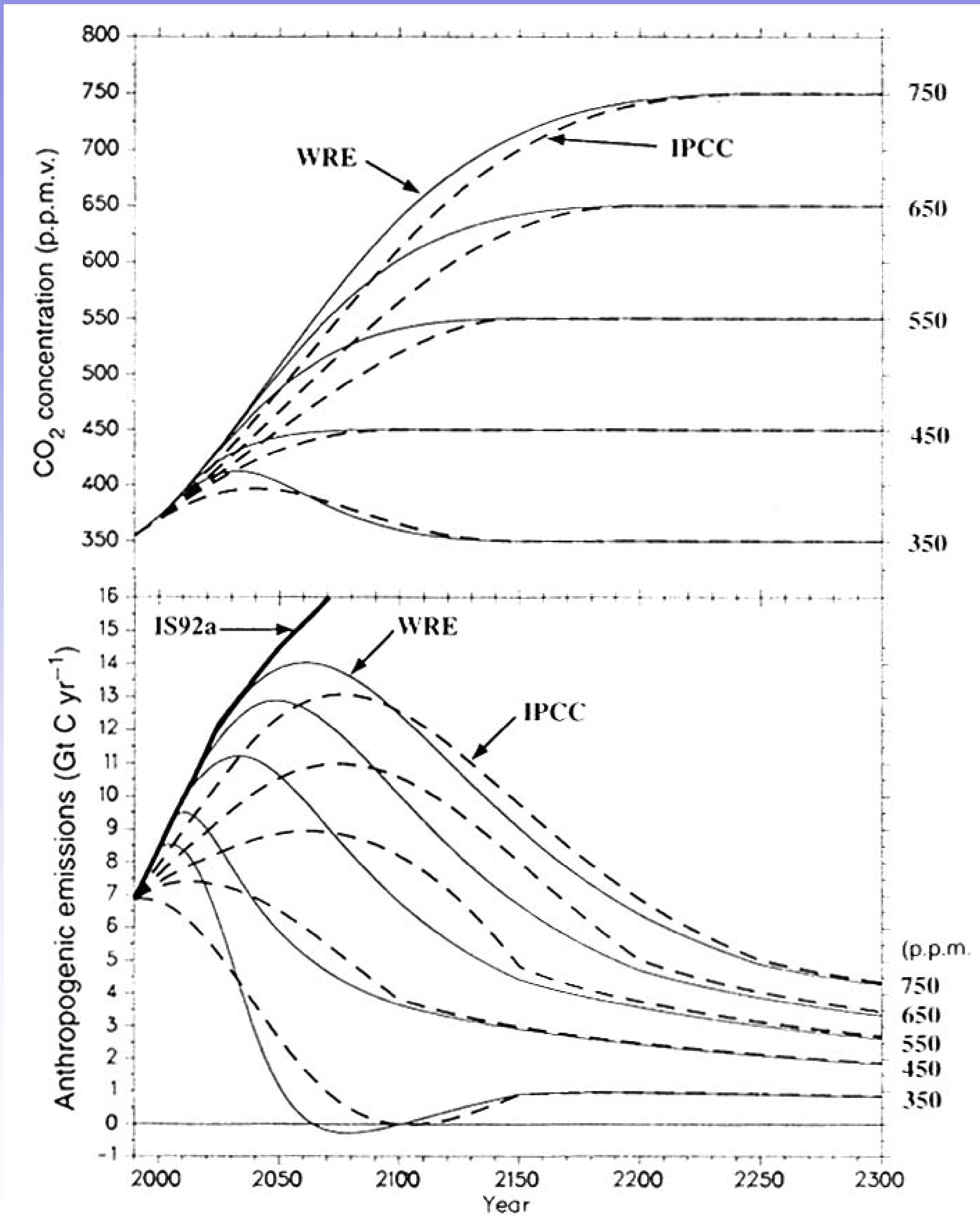


- *From Wigley et al. (1996)*

- ***Emission trajectories required to achieve stabilization of atmospheric CO_2 levels at various values incorporating "best" economic choices.***

- ***In order to achieve stabilization at 550 ppmv departures from current trends of about 3.67 billion tons of CO_2 per year are required by 2025, and about 14.7 billion tons per year by 2050.***

- ***This may be achieved by conservation, substitution, or sequestration strategies.***

The evolving chemistry of surface sea water under "Business as Usual"

Time	pCO_2	Total CO_2	pH	HCO_3^-	CO_3^{2-}	H_2CO_3
yr.	µatm	µmol kg^{-1}		µmol kg^{-1}	µmol kg^{-1}	µmol kg^{-1}
1800	280	2017	8.191	1789	217	10.5
1996	360	2067	8.101	1869	184	13.5
2020	440	2105	8.028	1928	161	16.5
2040	510	2131	7.972	1968	144	19.1
2060	600	2158	7.911	2008	128	22.5
2080	700	2182	7.851	2043	113	26.2
2100	850	2212	7.775	2083	97	31.8

Under IPCC "Business as Usual" the pH of surface sea water drops by 0.4 pH units by 2100. $CO_3^=$ in surface water drops by 55% from pre-1800 values. It will be hard to meet even these goals.

MBARI

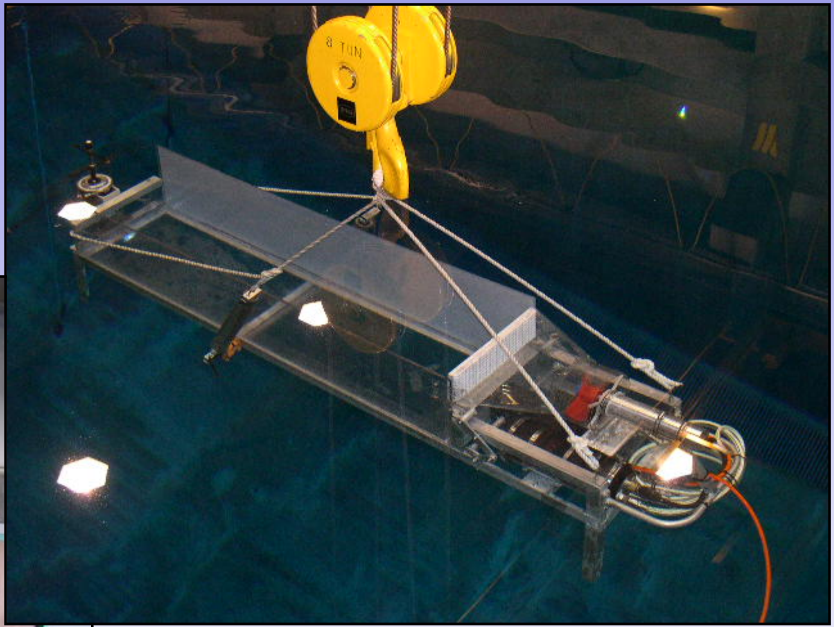
MBARI Small-scale CO_2 experiments

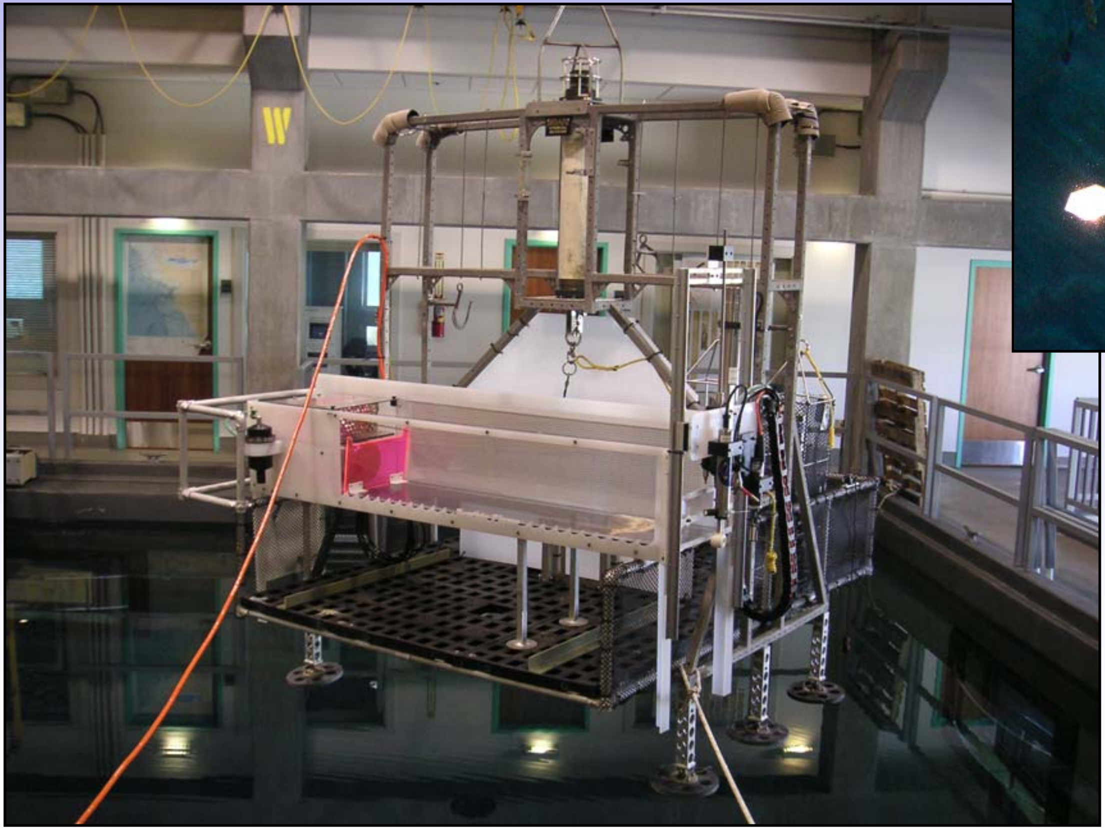
- We have been doing small-scale CO_2 release experiments since 1996:
  - Kinetics of CO_2 & CH_4 hydrate formation.
  - Rates of liquid CO_2 & CO_2 hydrate dissolution.
  - Amount and extent of pH disturbances.
  - In collaboration with biologists (J. Barry and M. Tamburri), have looked at the impact on biota.
- Problems:
  - Limited control of experimental conditions.
  - Observed novel but not reproducible results.

OACE Research Interests

- MBARI:
  - Develop and deploy new technology for controlled seafloor CO_2 release experiments.
  - Liquid CO_2 and CO_2 hydrate dissolution rates.
  - CO_2 hydration / dehydration kinetics.
- University of Bergen:
  - Fluid-dynamics & chemistry of liquid CO_2 in deep sea.
- NMRI:
  - Develop and conduct pressure tank experiments.
  - Hydrate skin strength and growth rates.
  - Liquid CO_2 / sediment interactions.

Benthic Flume





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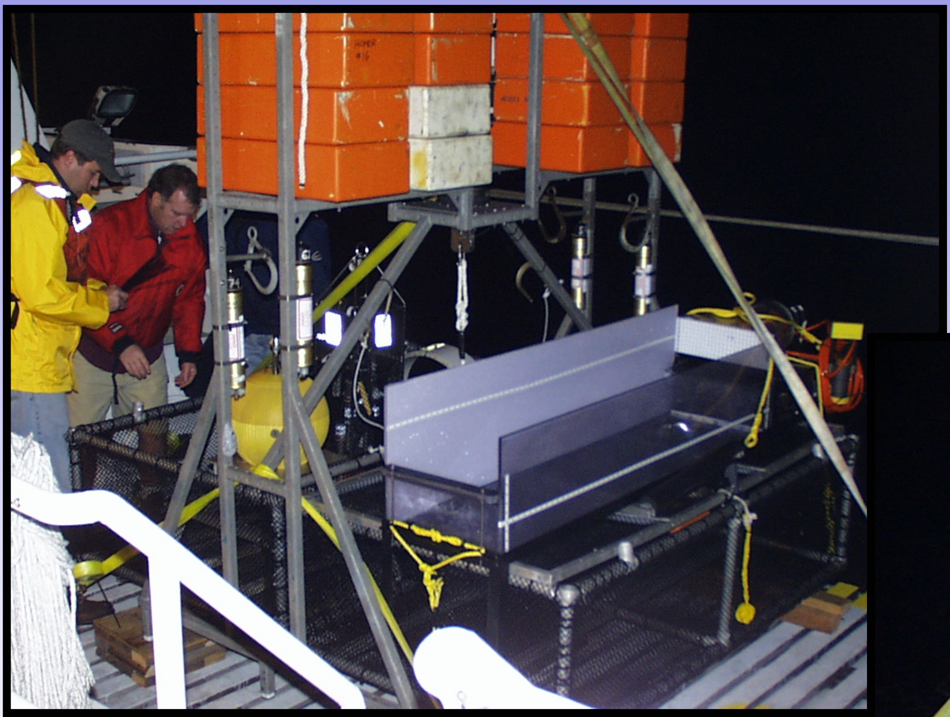
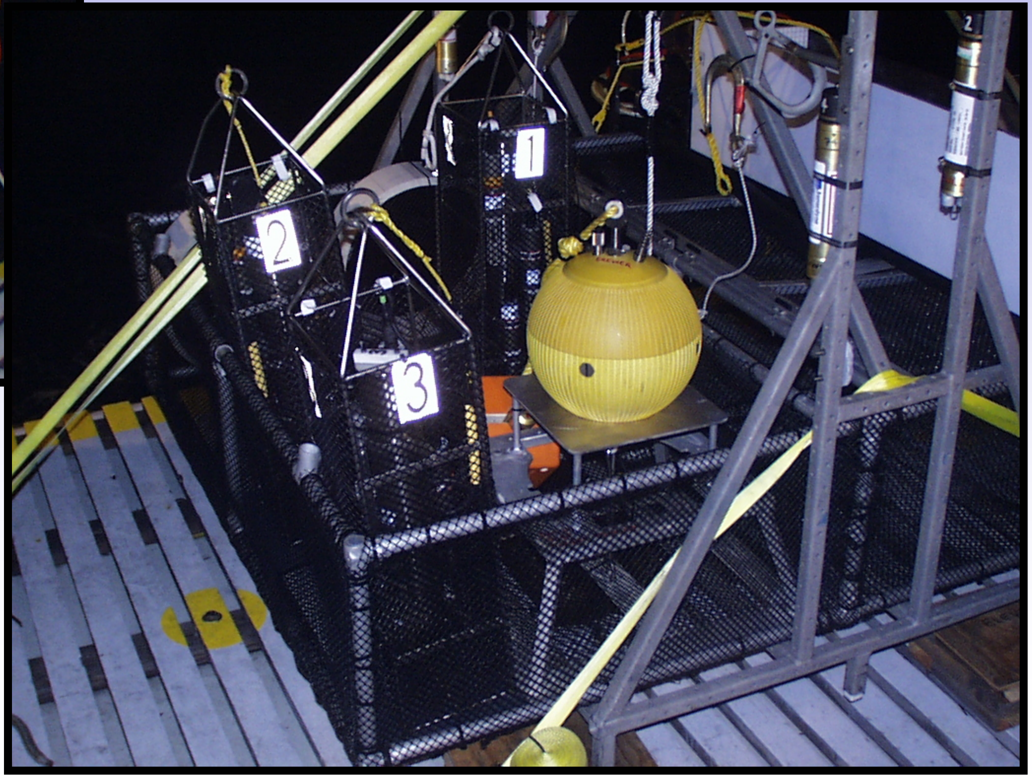
Equipment elevator





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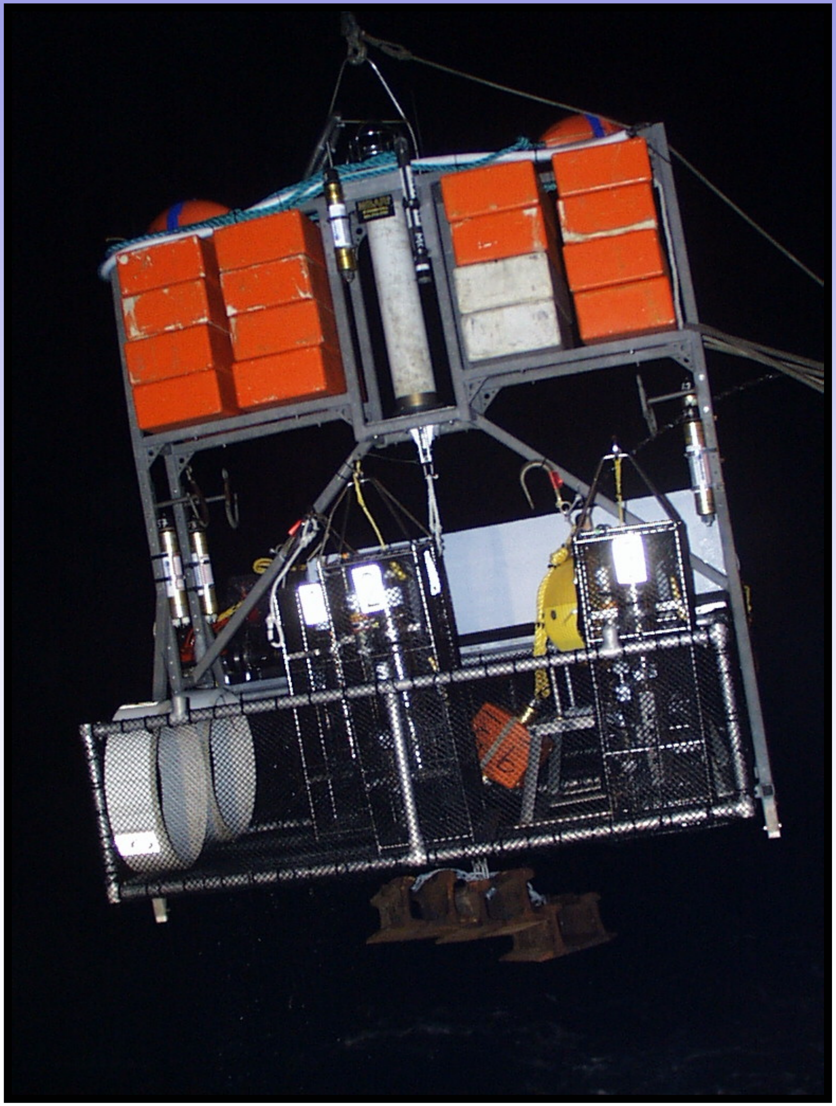
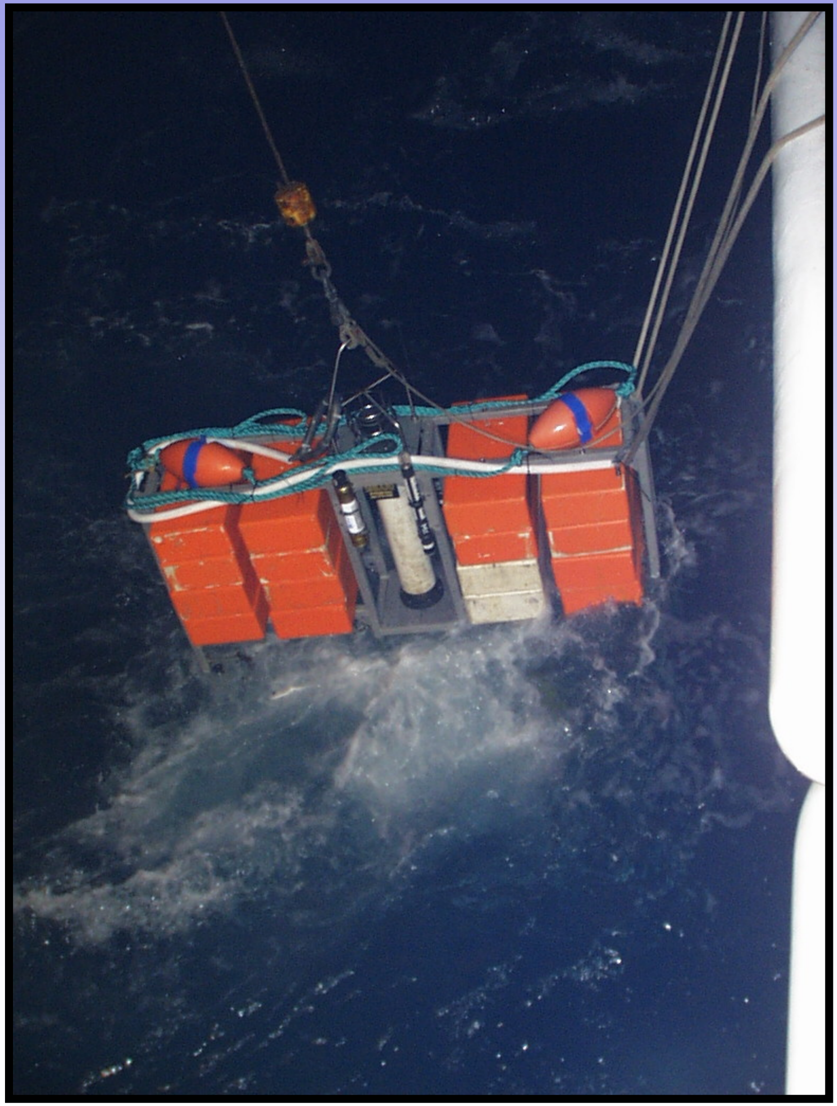
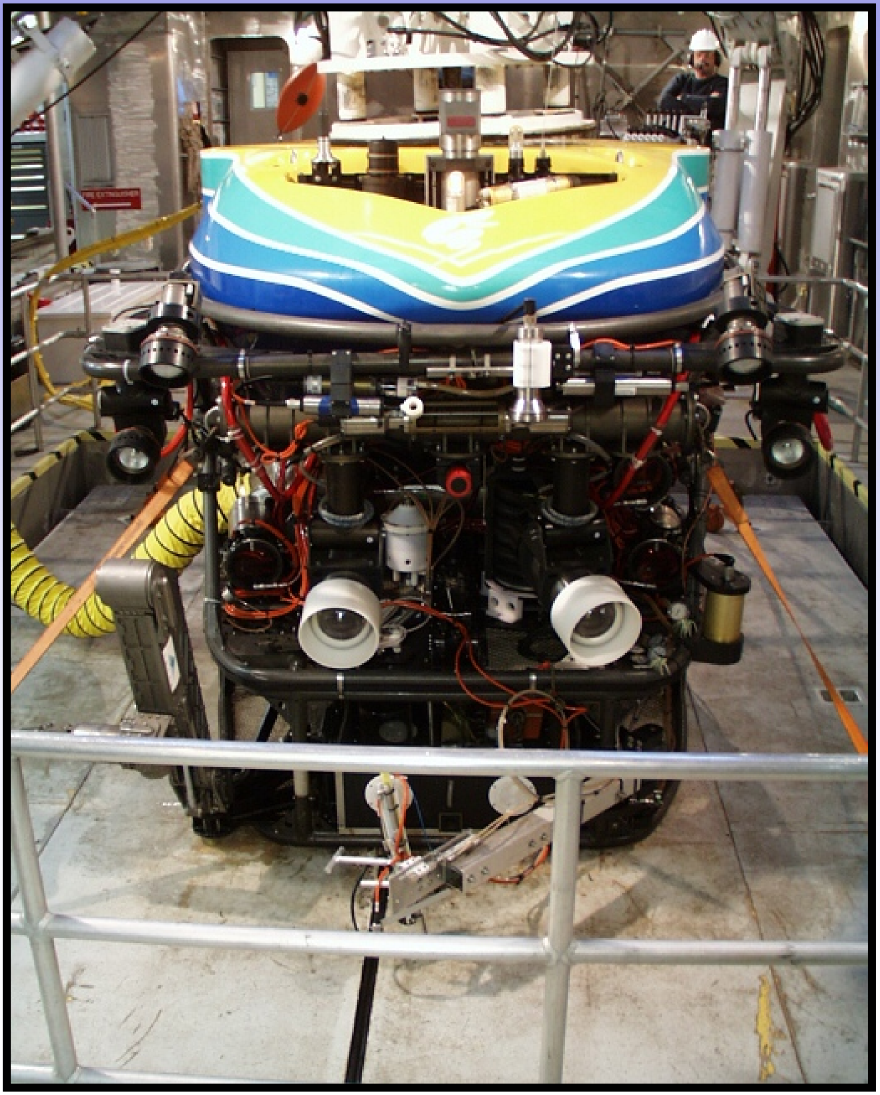
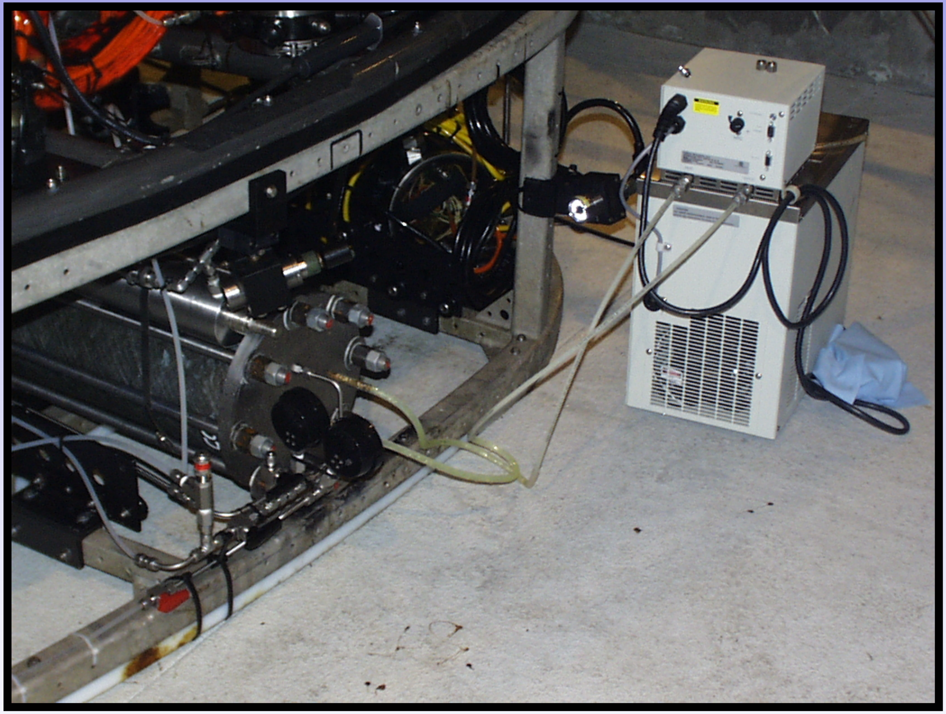
Elevator deployment





ROV Tiburon





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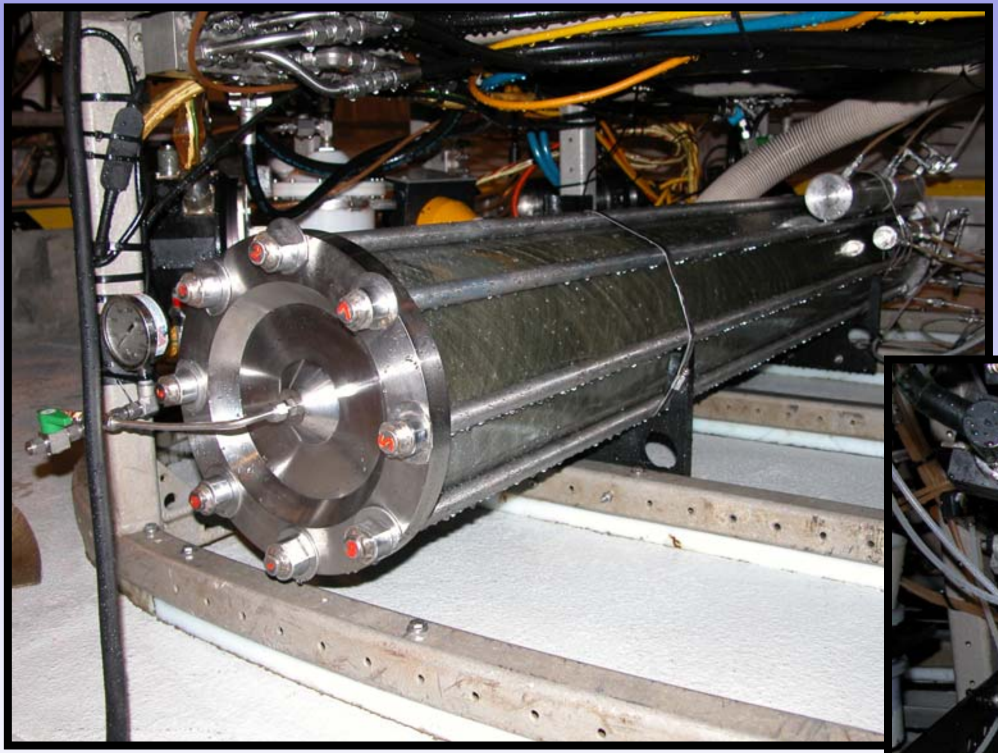
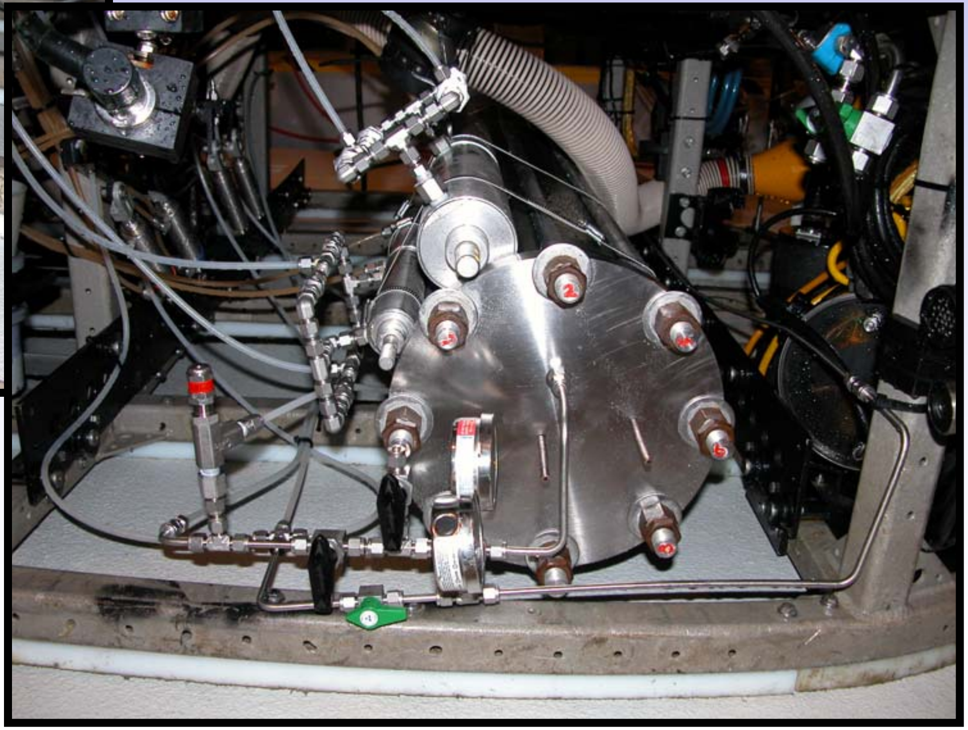
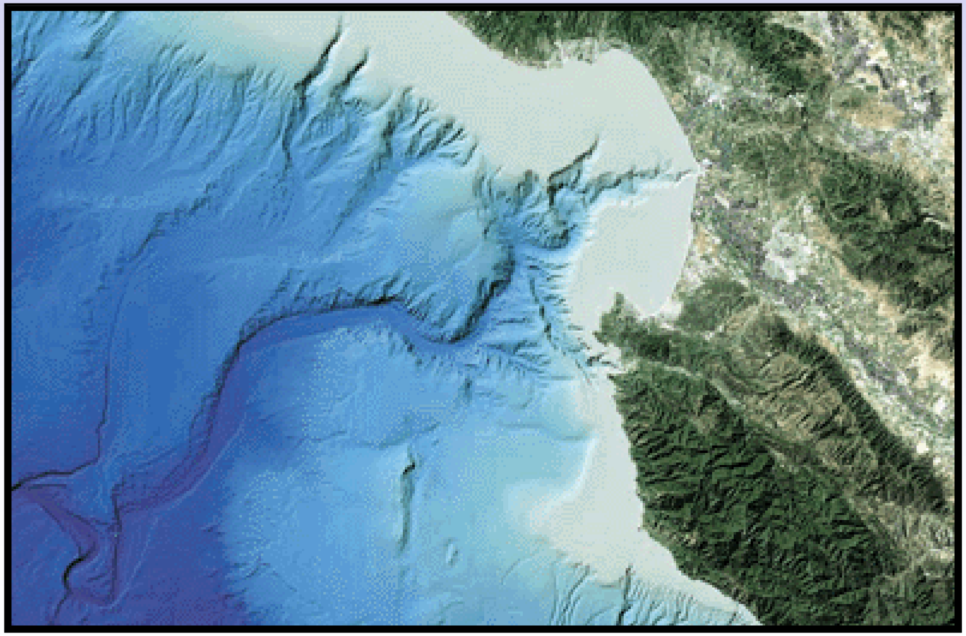
56L CO2 Accumulator



- SW side
- CO_2 side



Experiment conducted in Monterey Bay



Video Highlights

- Dye injection experiments at various flowrates.
  - pH indicating dye = phenol red.
  - yellow (6.6) ↔ red / purple (8.0).
- Wave generation by "bottom currents."
  - Slow flow → ripples.
  - Faster flow → breaking waves and droplets:

    "CO_2 spray"

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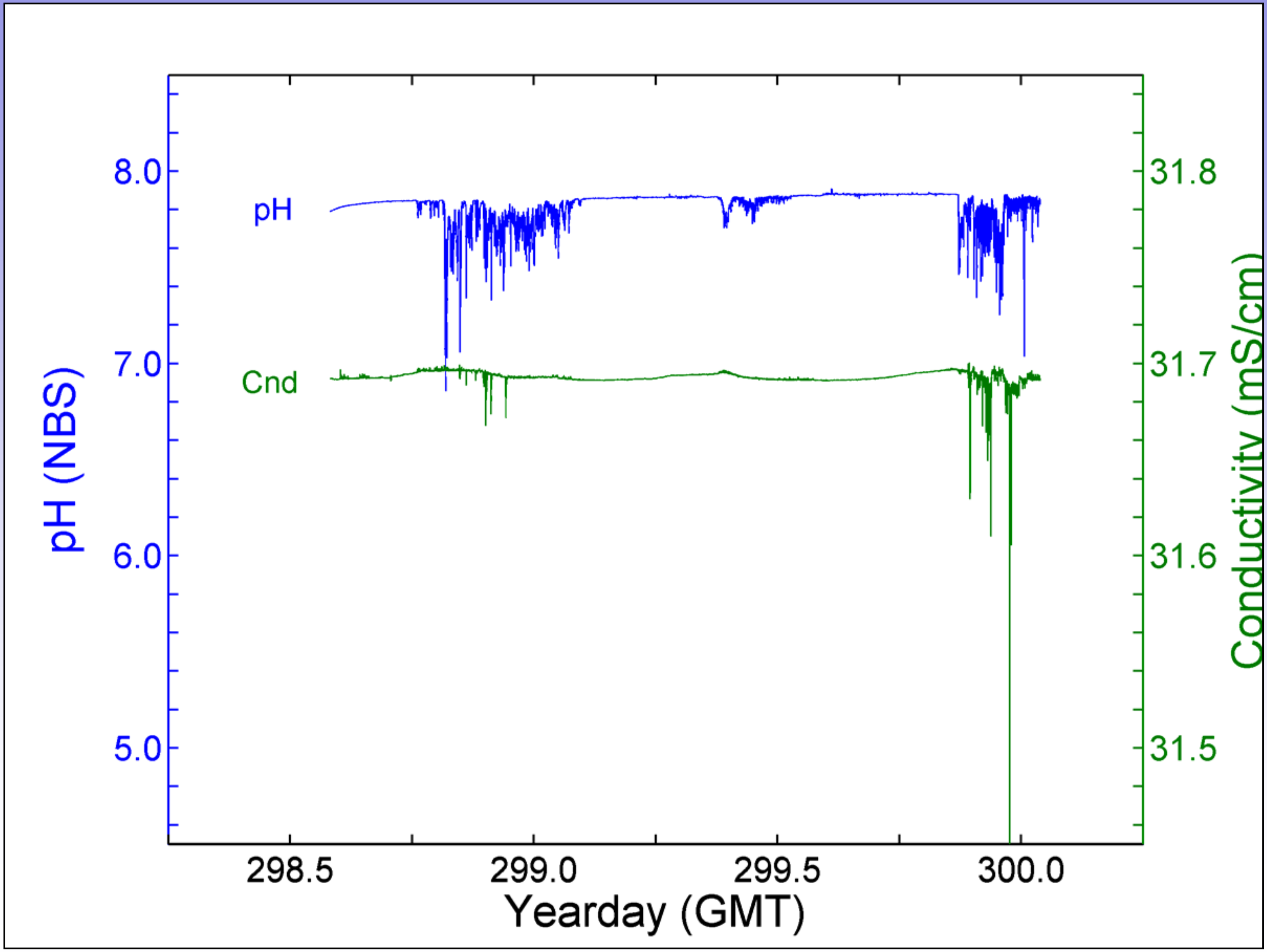
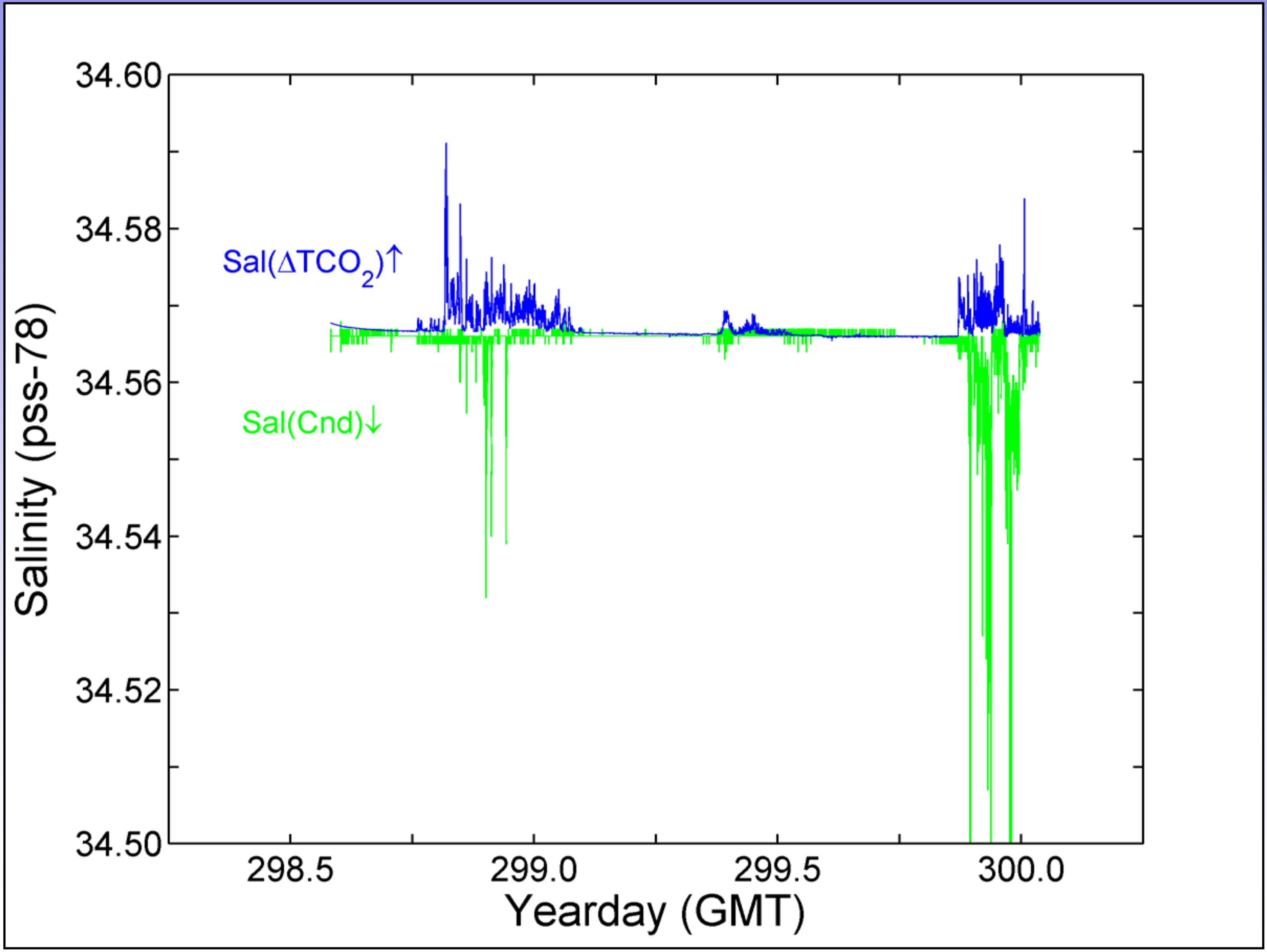
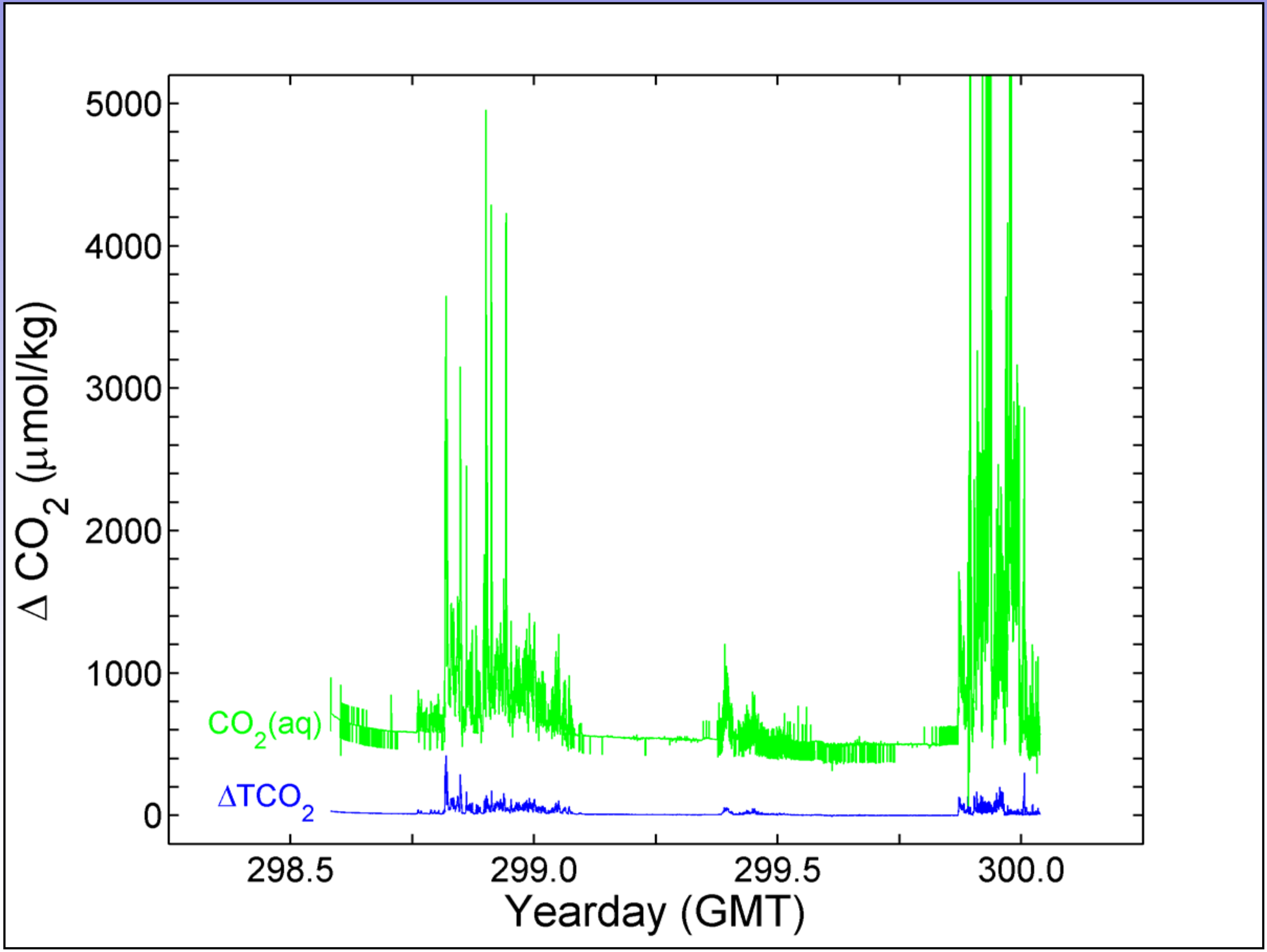
CTD data record downstream from flume.



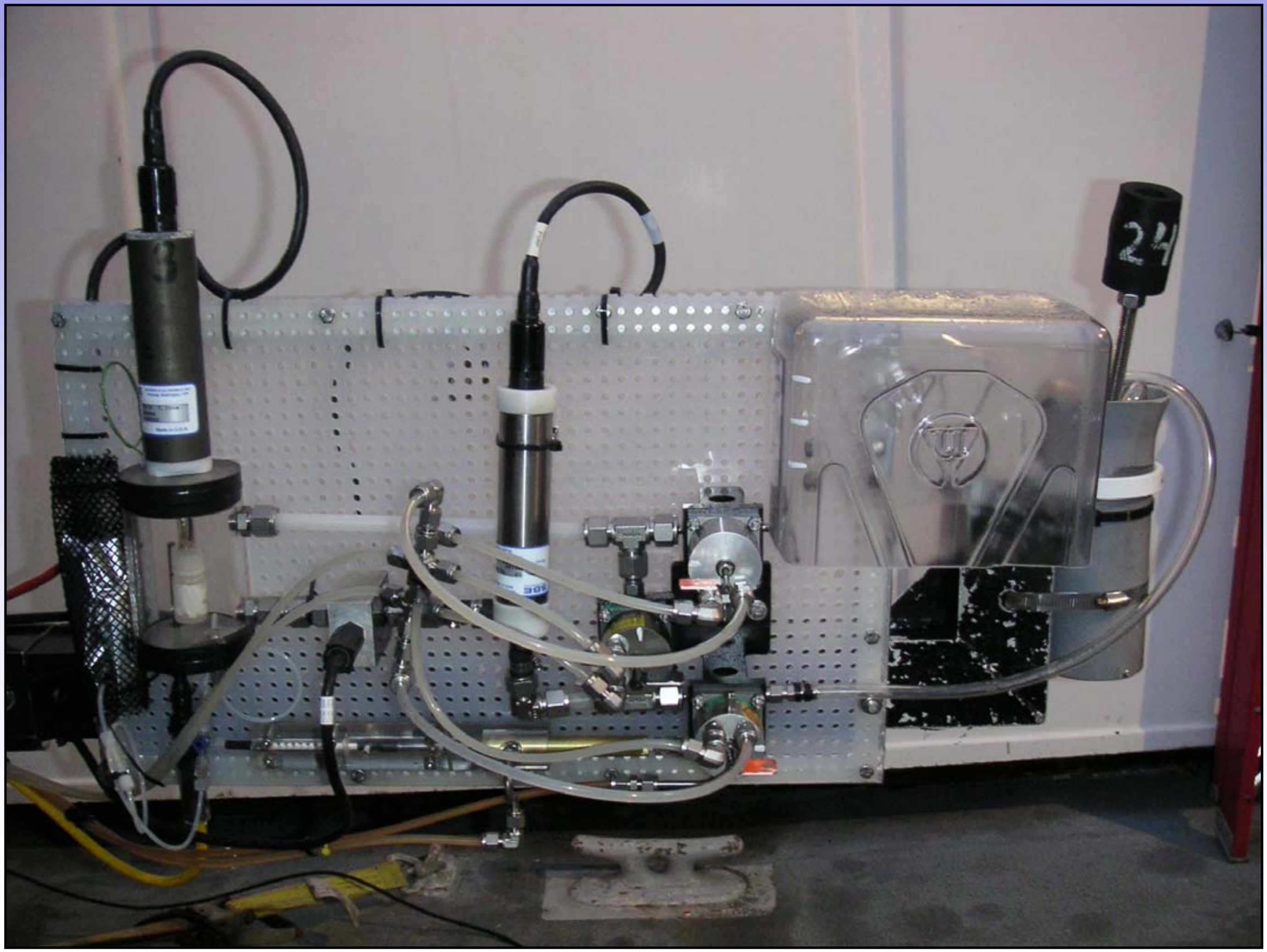
Salinity observed and calculated downstream from flume.



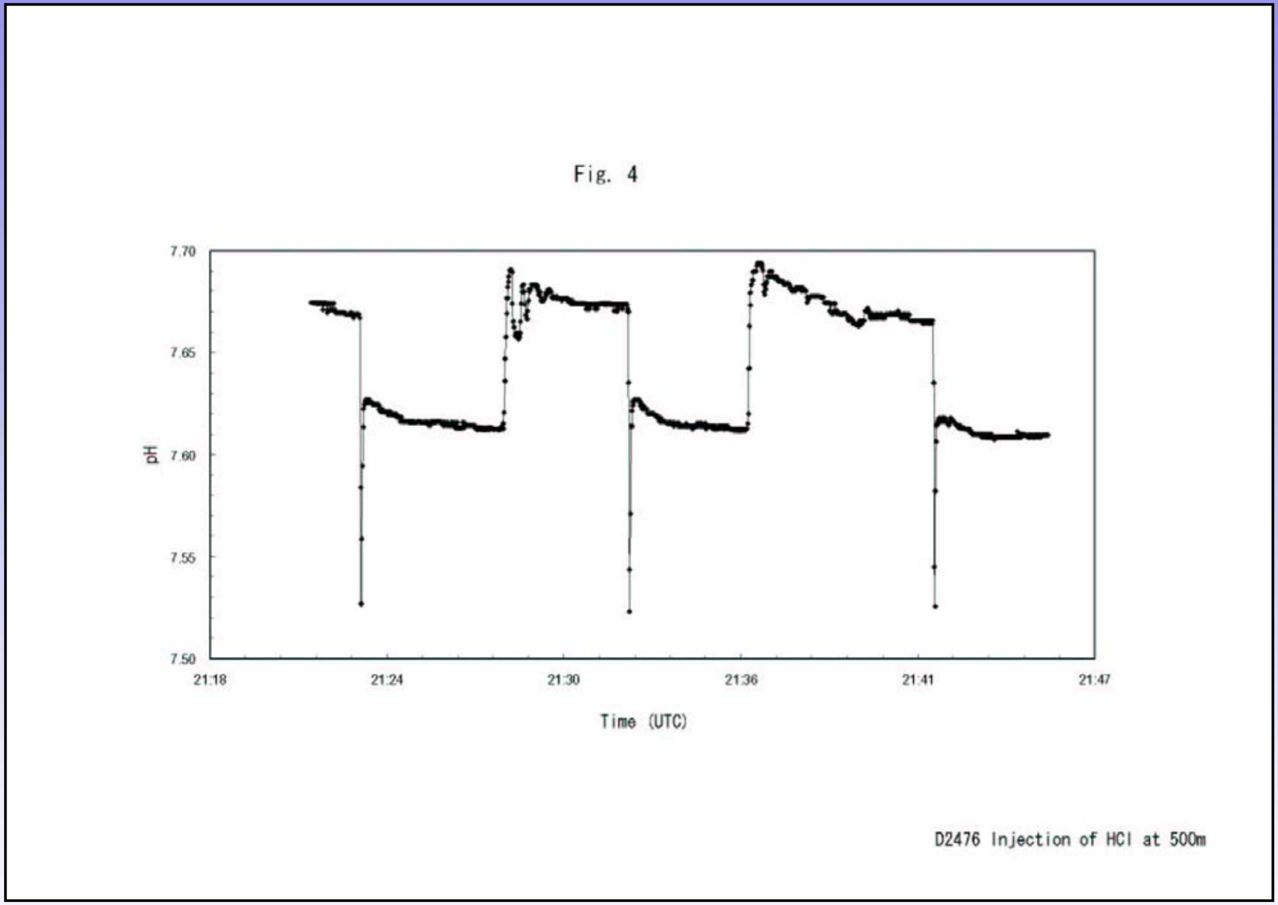
ΔCO_2 concentration downstream from flume.



Seawater re-circulation cell

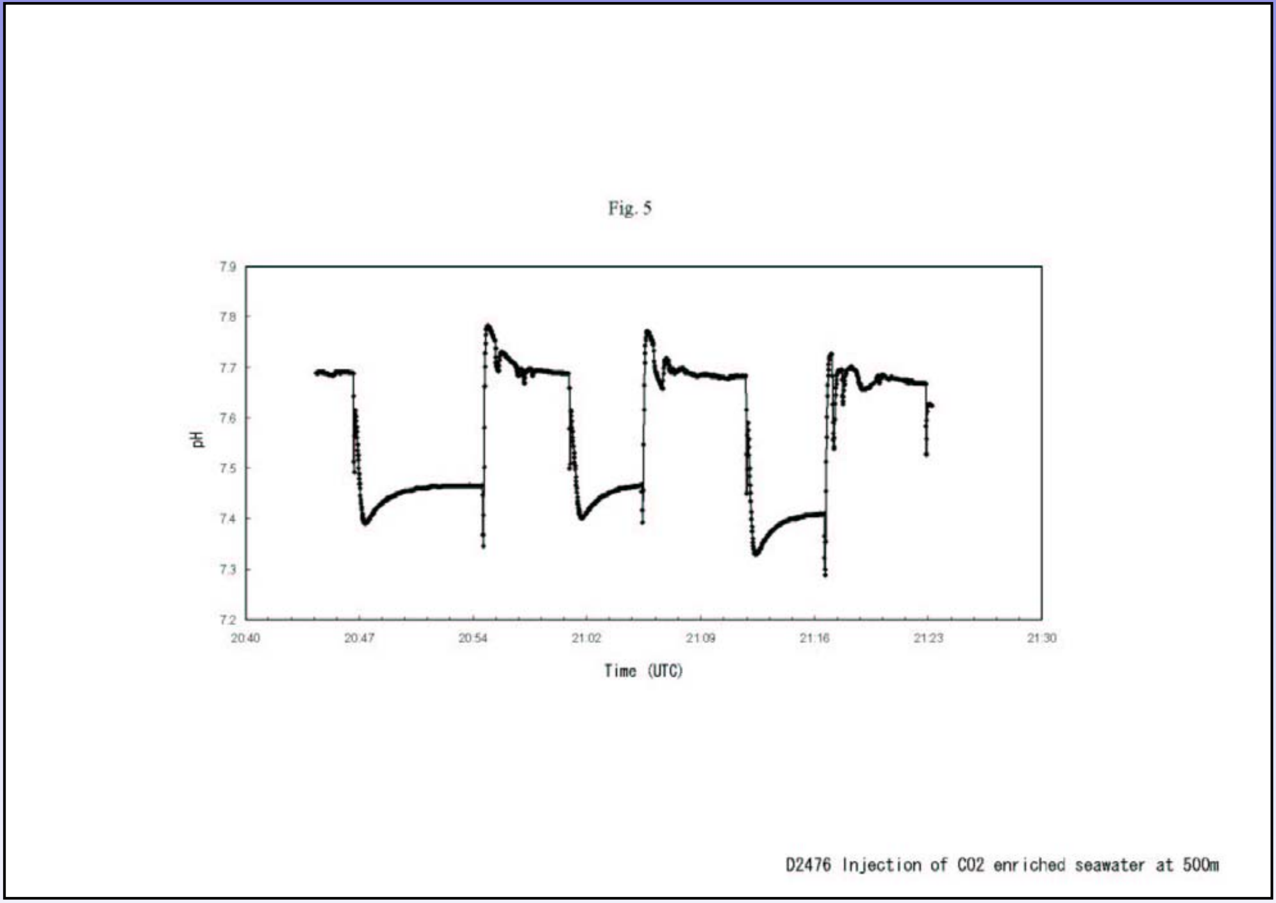


Results from a 500m depth acid injection experiment to test the feasibility of in situ controlled pH perturbation experiments.



The data are consistent with formation of an intense cloud of CO_2 at the injection tip, followed by rapid mixing and hydration of the excess CO_2 to form HCO_3^-. This reaction has a volume decrease, and is accelerated by pressure.

Results from an injection of HCO_3^- rich water in contact with a CO_2 pool.



The shape of the curve differs from acid injection and is consistent with removal of excess HCO_3^- . This requires a volume increase, and the reaction at depth is slower than for acid addition – but still far faster than at 1 atm.

pH versus time curves for an experiment at 500m depth (6°C) for both acid addition (upper left) and HCO_3^- rich water addition (lower right).

The initial rapid change is not fit, only the slower exponential decay at the end.

Note the reversed shape, and the slower response of the HCO_3^- curve.

Fig.A

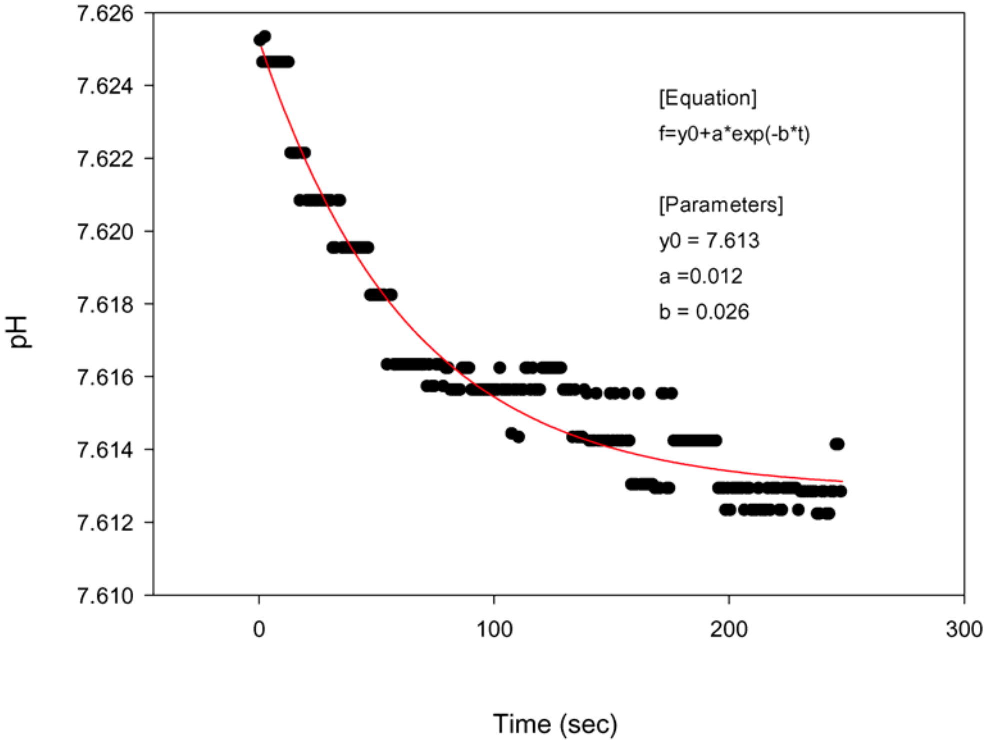
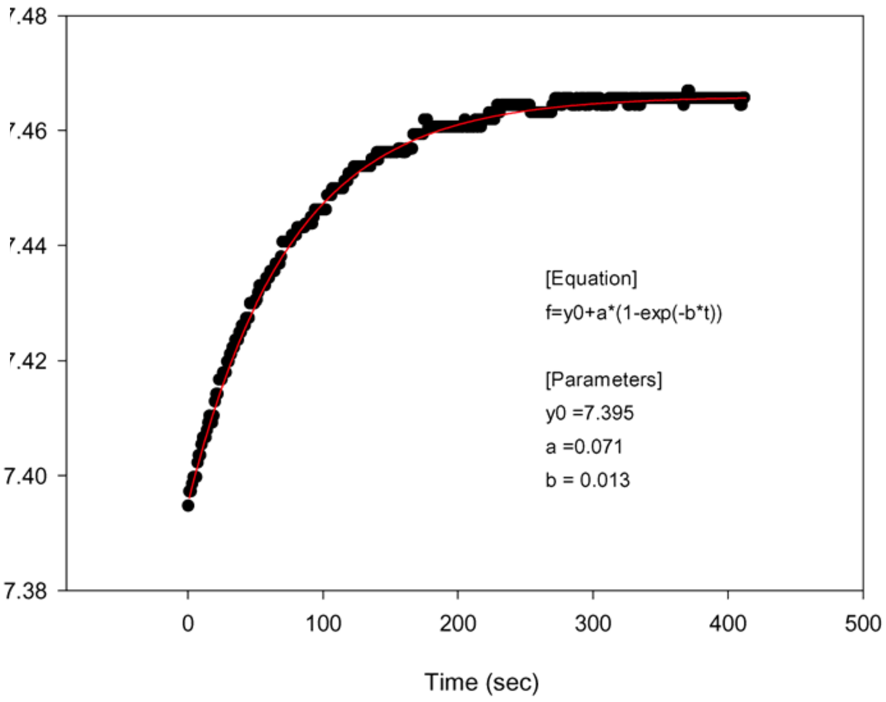
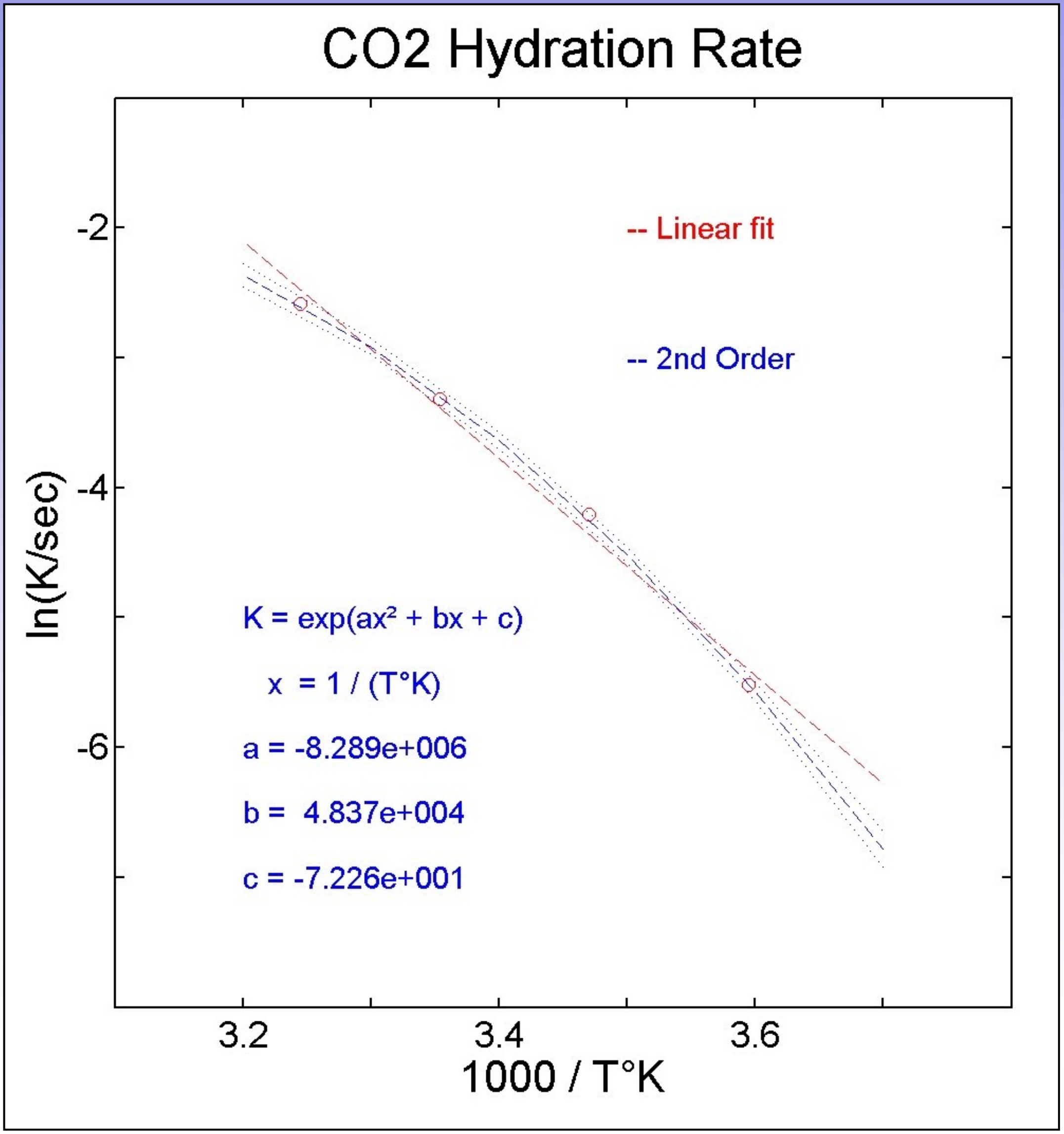
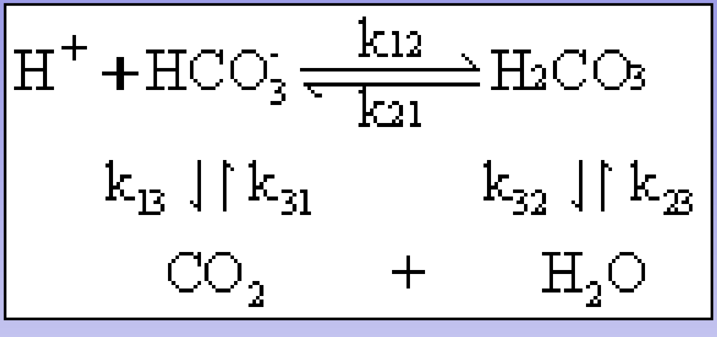


Fig. B



The CO_2 hydration rate constant (Johnson,1982)

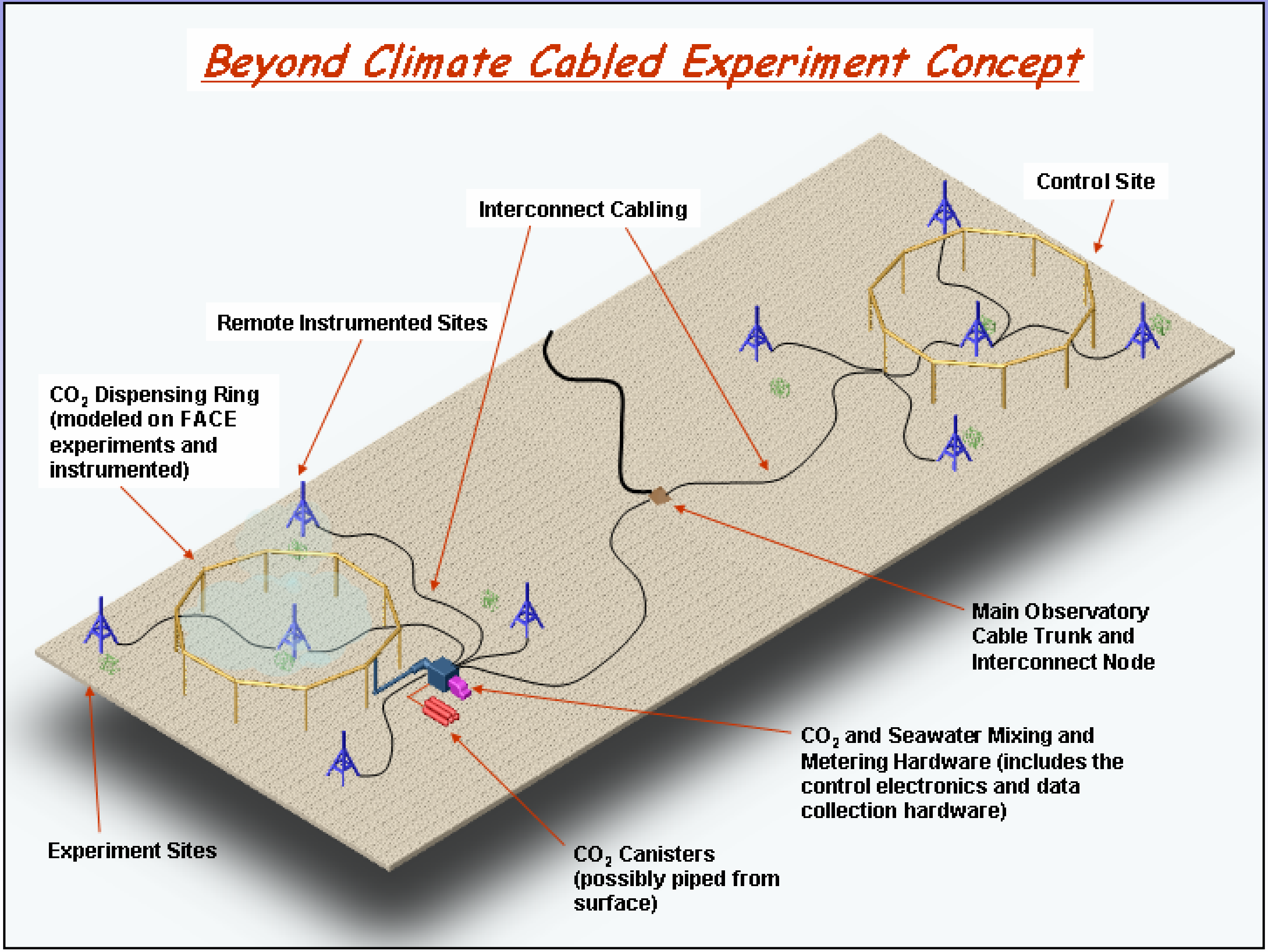




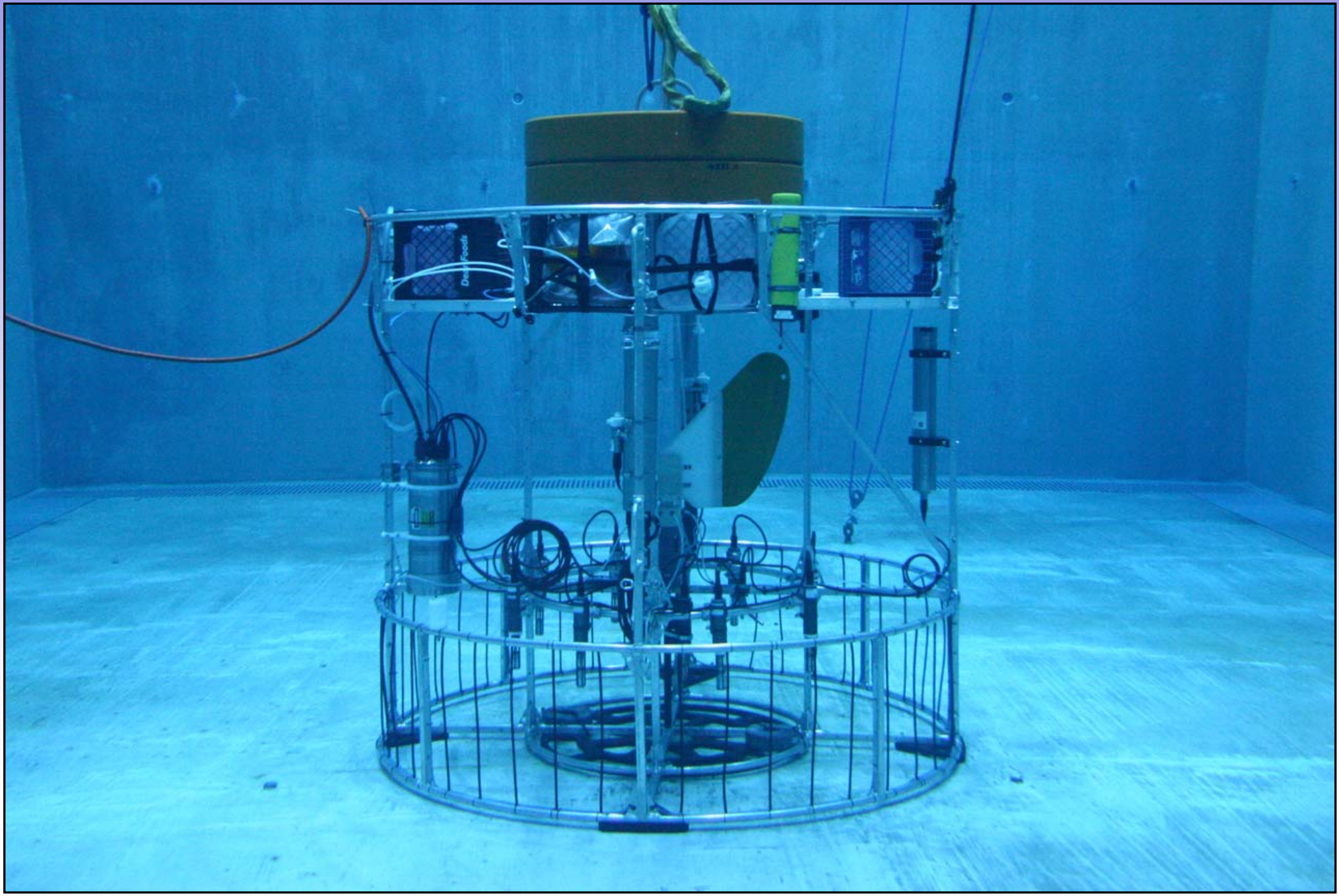
These data are for 1 atmos. They imply a time to equilibrium of ~32 minutes at 1.6°C, and 17 minutes at 6°C; this rxtn time is far beyond our observations.

However the dissolution of CO_2 produces a strong -Δ V, and thus the effect of pressure is to shift the equilibrium to the hydrated state – but the <u>rates</u> at pressure are unknown.

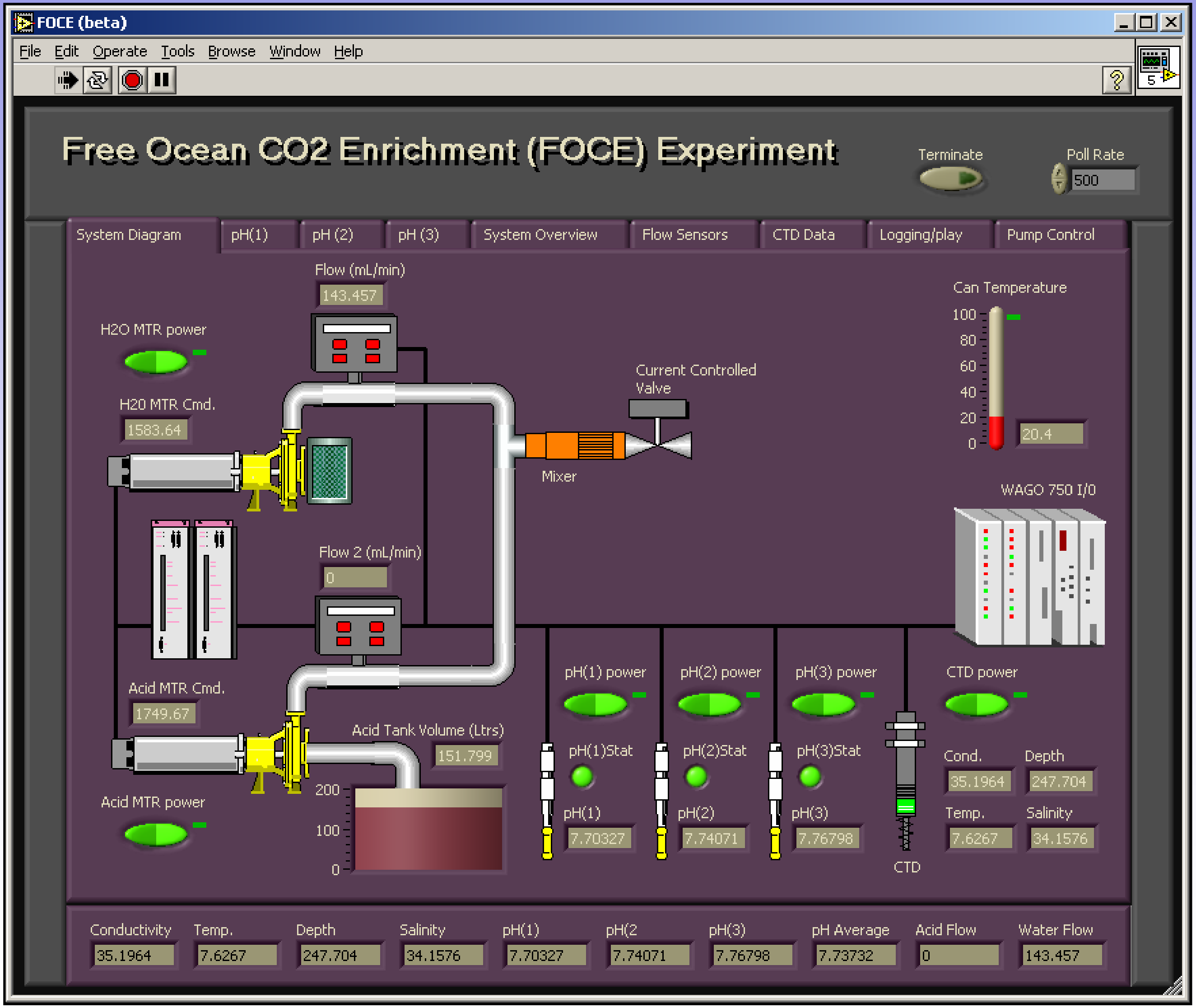
If we are to understand the science of a lower pH ocean we have to carry out predictive experiments. A concept sketch is shown here with supply of either acid or CO_2 to a set of experimental sites in much the same way that experiments are carried out on land. There are fundamental challenges in this.



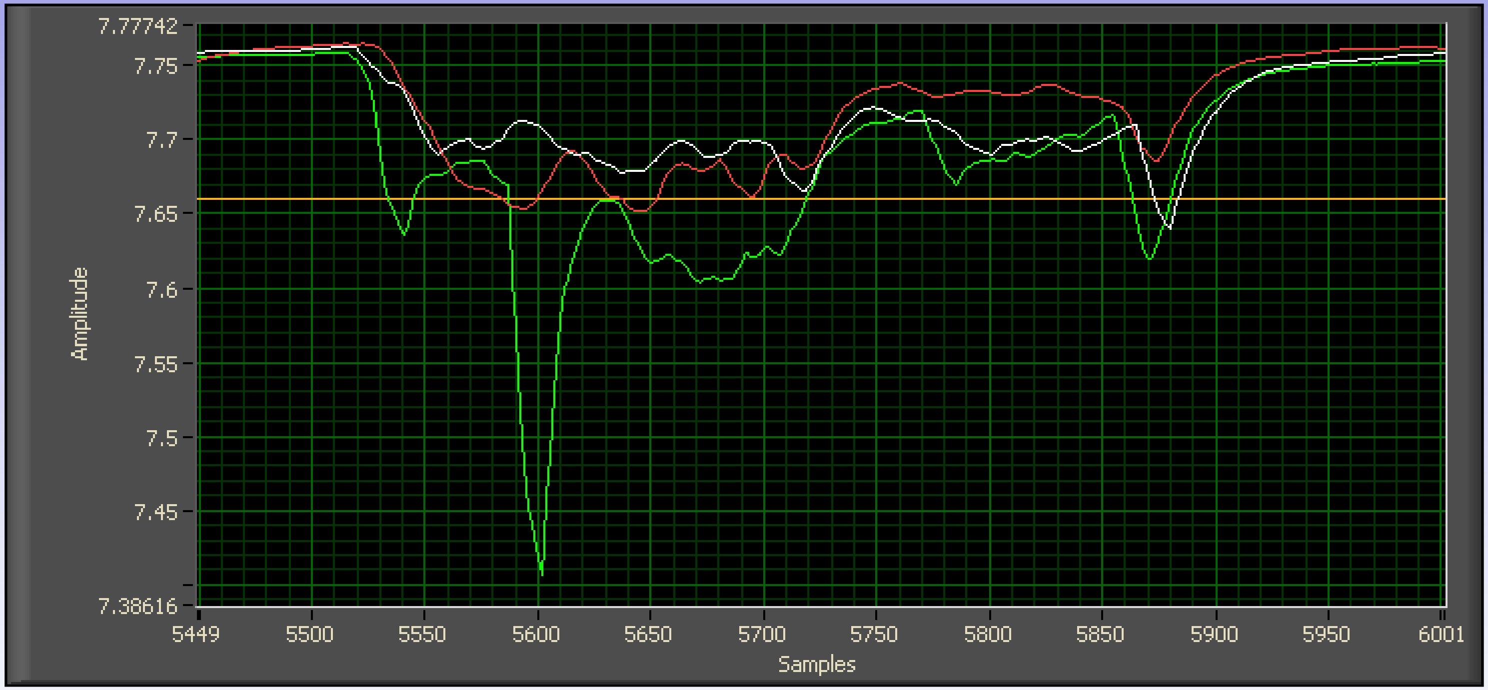
FOCE Prototype



FOCE Prototype Control GUI



Example data – First FOCE Prototype Deployment – April 2005



White/red/green are top/mid/bottom sensors.

Orange is the pH control set-point.

Acknowledgements

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